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POTENTIAL APPLICATIONS OF ALKALI-ACTIVATED ALUMINO-SILICATE BINDERS IN MILITARY OPERATIONS

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A preliminary study was undertaken to evaluate the potential applications of alkali-activated alumino-silicate binders in military operations. Alkali-activated binders are produced by mixing a concentrated alkali-solution (such as potassium or sodium hydroxide) with a fine-grained, non-crystalline alumino-silicate (such as granulated slag or fired clay). The resulting reaction is reported to produce a series of calcium hydrosilicates (tobermorites) and mixed calcium sodium aluminum silicates (zeolites) and hydrogarnets. The

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hardened binder shows exceptionally strong bonding to aggregate and the binder/aggregate mixes have been reported to show as much as 27 MPa or 4,000 psi unconfined compressive strength in four hours. Strengths as high as 175 MPa or 25,000 psi can be developed in 28 days. Heats of reaction are very low and external heating is usually needed to insure rapid curing. Alkali-activated binders usually have low water content, high density and low permeability. Sulfate resistance is high and the binder does not accelerate corrosion of reinforcing steel.

An alumino-silicate binder that can be cured to develop high early strength and good bonding characteristics may be adaptable to Army repair and construction needs. Major areas that are identified as requiring special construction materials are repair of lines of communication including repair and restoration of paved surfaces such as roadways, runways and bridge decking and the construction of roads and airfields. Rapid-setting high-strength binders could also be employed in movement of military traffic over beaches and soft soil.

Alkali-activated binders have a number of properties that make them potentially useful for expedient construction and repair. Raw materials are stable in storage and can be used with substandard aggregate without loss of strength. A minimum of make-up water is required and water quality is relatively unimportant (salt water can be used if necessary). Bonding to materials other than asphalt is excellent. Alkali-activated binders have low toxicity and require no organic solvents for mixing or clean-up. Most equipment used to handle portland cement concrete can be made to operate with alkali-activated binders. Heat curing allows the binder to be placed under adverse conditions.

A small-scale pavement patching demonstration using a commercially developed alkali-activated binder showed that a 1.62 × 1.62 m pavement patch (18-cm-thick) could be placed and cured in four hours and would develop sufficient strength to carry a 12.2 metric ton load on a F4 fighter wheel.

PREFACE

This study was conducted by the US Army Engineer Waterways Experiment Station (WES) for the Assistant Secretary of the Army (R&D) as an In-House Laboratory Independent Research (ILIR) Project under Project No. 4A161101A91D, Task Area 02, Work Unit 155. Part IV of this report was prepared by Pyrament N. V. under Contract No. DACW 39-84-M-4612 dated 14 September 1984.

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Mr. Samuel J. Alford (Geotechnical Laboratory) assisted in preparing a prototype pavement repair.

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POTENTIAL APPLICATIONS OF ALKALI-ACTIVATED ALUMINO-SILICATE BINDERS IN MILITARY OPERATIONS

PART I: INTRODUCTION

Background

1. Alkali-activated, alumino-silicate binders are a family of cementitious materials that are formed by reacting a fine-grained silica- and alumina-rich solids with a solution of alkali or alkali salts. The two (or more)-component mix reacts (with or without heating) to produce a series of gels and crystalline compounds that form a new hardened matrix. Difficulties arise in describing the general product because a wide variety of materials (slag, fly ash, ground rock, etc.) can be used as the source of silica and alumina and many different alkaline solutions (or salts) can be used to produce the hardening reaction. The unusual properties of the alkali-activated products include very high early strengths (as much as 27 MPa or 4,000 psi unconfined compressive strength after moist heat curing for four hours) and high ultimate strengths (as much as 175 MPa or 25,000 psi in 28 days). Further, the heat of reaction for an alkali-activated setting reaction is very low, 25-50 percent of that of conventional portland cement-based binders, thus the application of external heating is commonly used to accelerate setting. Without heating, the strength and set times are approximately those obtained with a typical portland cement-based binder (Glukhovskii, et al. 1967; Forss 1981, 1982, 1983).

2. Alkali-activated binders are typically made with low water content (water/solid ratios of 0.2-0.3) and may have very little entrained air (0.5-1.5 percent). Alkali-activated binders still retain excellent freeze-thaw durability due to their density and low permeability. Sulfate resistance is very high for the same reasons. Although the pH levels of alkali-activated binders are high (pH 13-14), carbonation (reaction with carbon dioxide in the air) is minor due to the high density of the hardened binder.

3. The reaction in alkali-activated binders will take place with a wide variety of silicate and/or aluminum-rich minerals and glasses, therefore many

different fine-grained alumino-silicates (clay, ground rock, ash, slag) can be used as raw materials. For the same reason, alkali-activated binders form strong bonds with poorly washed or clayey aggregate. The alkali concentration in the reaction water is sufficiently high that most natural waters cannot interfere wit˙ the binder reactions.

4. 1 tolerant character of alkali-activated alumino-silicate reactions and the speed and strength of set make this binder system especially interesting for military applications, where a wide variety of materials may have to be substituted in the binder and the available aggregate may not be up to standard. Alkali-activated binders require some modifications in mixing, placing, and curing practices, but the versatility and speed of setting make it worth learning how to work with these alternate binders.

Purpose

5. The purpose of this report is to present basic information on alkali-activated silico-aluminate binder systems and to discuss the Army needs and areas of potential applications of these binders in solving Army problems.

PART II: USE OF ALKALI-ACTIVATED ALUMINO-SILICATE BINDERS

Development of Alkali-Activation Technology

6. Alkalis, such as sodium or potassium hydroxide, were originally used in the 1930's to test ground slag to determine if the slag would set when added to portland cement. In the course of studying the testing system for slag, Purdon (1940) discovered that the alkali addition produced a new, rapid-hardening binder. In a mortar mix consisting of one part binder and three parts sand, the alkali-activated slag developed strength faster than either rapid-hardening portland or ordinary portland cement. The initial studies performed by Purdon were restricted to sodium hydroxide and sodium salts reacted with selected Belgian metallurgical slags. Purdon realized that a sodium salt and lime (calcium hydroxide) had the same hardening effect as did sodium hydroxide. Purdon mentioned several important considerations in using alkali-activated slags as binders:

- a. Cost could be very low where slag is a waste product.
- b. The binder gained strength rapidly offering great advantages in precasting operations.
- c. The binder had very low heat of hydration and was not stressed thermally during hardening.
- d. The hardened binder was more watertight and less soluble than portland cement hydrate.
- e. No corrosion of iron reinforcing bar occurred in hardened binder.
- f. The binder could be made up using sea water and the sodium salts in the water became part of the activating solution.

7. Major problems in the use of alkali-activation are:

- a. A liquid caustic solution containing 6-7 percent NaOH was required for activation.
- b. Slag mixed with lime and sodium carbonate could be used with water as the only additive, but the lime reacted with carbon dioxide during storage and became inactive.

8. Alkali-activated slag cements (called Trief cements) were used in large-scale construction as early as the 1950's. The usual activation called for adding 1.5 percent NaCl and 1.5 percent NaOH to 97 percent ground slag mix (U. S. Army Engineer Waterways Experiment Station 1953). The water/binder ratio was 0.5. Generally Trief cements were not heated during curing.

9. Early theories proposed by Purdon stated that the action of sodium hydroxide was largely catalytic and that the sodium did not end up in any crystalline phase produced in hardening. The sodium was thought to make the glassy material in the slags dissolve and react more rapidly than would be possible in water. Predominantly calcium silicate hydrates were thought to form from the slag glasses. Purdon (1940) summarized the action of sodium hydroxide as consisting of two steps (Figure 1):

a. Liberation of silica, alumina and lime by sodium hydroxide solution.

b. Formation of hydrated calcium silicates and aluminates and regeneration of the sodium hydroxide (caustic) solution.

As support for this theory, Purdon pointed out that it is possible to leach sodium hydroxide out of the hardened alkali-activated binder in approximately the amounts the alkali is added. Further, Purdon pointed out that although the rate of strength-gain of binders containing small amounts of sodium hydroxide was low, eventually even these binders reached high ultimate strength. Once the reaction was started, hardening and strength development proceeded without any additional alkali.

10. Glukhovskii investigated the problem of alkali-activated slag binders in the 1960's and 1970's and made major contributions in:

a. Demonstrating that sodium salts, such as phosphates, fluorides and carbonates could be used as activators.

b. Identifying both calcium silicate hydrates, and calcium and sodium alumino-silicate hydrates (zeolites) as solidification products.

c. Demonstrating the effects of heating in producing high early strength.

d. Noting that clay minerals react during alkali treatment to form sodium aluminum silicate hydrates (zeolites).

By the 1960's, alkali-activated slag cement were being used in Russia to produce concrete pipe, tunnel linings, walls, decks and structural beams and pilings (Glukhovskii 1974; Glukhovskii, Rostovskava and Rumyna 1980).

11. Russian research into alkali-activated slag reactions continued in the 1970's and 1980's and a better understanding of the setting reactions was obtained. The actual hardening process is now considered to be more complex than Purdon had proposed. Alkali attack on calcium-rich glass (slag) is thought to proceed with initial leaching of alkali (sodium and potassium) and

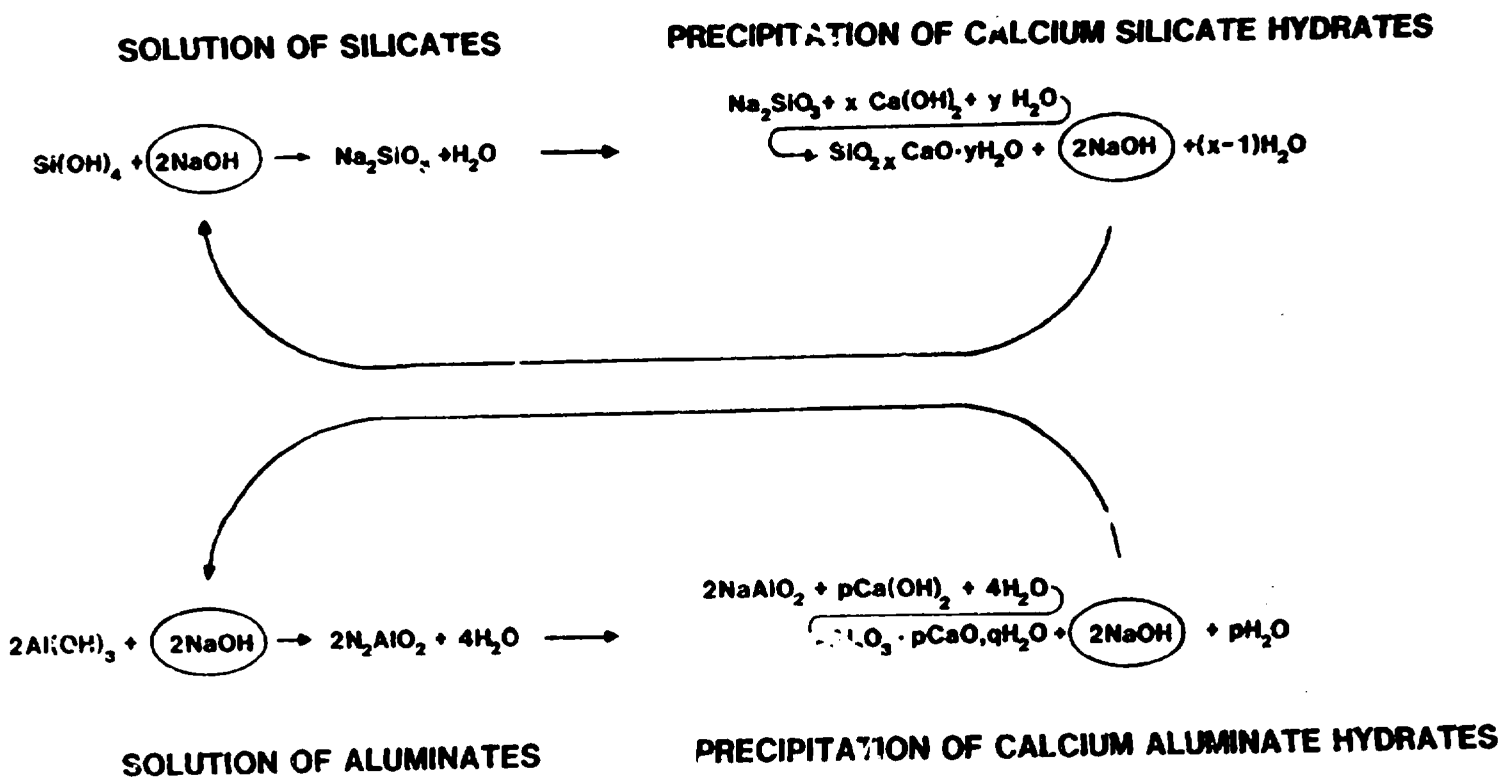

Figure 1. Reaction mechanism for alkali-activated alumino-silicate hardening proposed by Purdon (1940)

alkali-earth (calcium and magnesium) cations into solution and the formation of a colloidal sodium silicate layer on the solid glassy particles. Aluminum oxides dissolve directly in the sodium silicate (Kudryavtsev, Shkol'nik, and Ermakov 1977).

12. The first "minerals" tc form are weakly crystalline calcium hydrosilicates of the tobermorite group. The general formula for tobermorite is $Ca_{10}(Si_{12}O_{31})(OH)_6 \cdot 8H_2O$. The tobermorites continue to form and hydrogarnets, calcium alumino-silicate hydrates with an approximate composition of $3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, begin to crystallize. As the gels begin to coalesce, bound water is expelled and the binder becomes relatively fluid and the silicate and aluminum hydrates begin to form zeolite-like products and later sodium zeolites. The tobermorite mineral, foshagite ($Ca_8(Si_6O_{17})(OH)_6$), crystallizes during the latter phase along with additional zeolites (Grankovskii, et al. 1982). Heat and moisture accelerate the formation of all crystalline phases. When heat is used, the first crystalline phases to appear are low-basicity calcium hydrosilicates, analcime and natrolite (sodium zeolites) and hydrogarnet. Later crystalline products consist of foshagite and additional zeolite-like products. (Grankovskii, et al. 1982).

13. Much of the strength in slag-alkali systems has been attributed to the strong crystallization contacts between zeolites and calcium hydrosilicates. The use of alkali activation produces a uniform dense binder with very little, fine-grained unreacted silicate (such as clay) that can interfere with bonding to aggregate. (Glukhovskii 1974; Grankovskii, et al. 1982; Boldyrev and Tumenez 1984; Talling 1983, 1985). Separate zeolite crystal phases have not always been clearly identified in X-ray diffraction studies of alkali-activated binders. Some investigators have indicated that mixed sodium-calcium hydrosilicates are formed rather than separate sodium or sodium-calcium alumino-silicates that can be identified as zeolites (Teoreanu and Puri 1975; Teoreanu, Georgescu and Puri 1980).

14. The role of zeolites and zeolite-like tobermorites in alkali-activated alumino-silicates is still not completely understood but research on reactions between zeolites and calcium hydroxide (lime) indicates that lime reacts with and converts zeolites to tobermorites (Mitsuda 1970). The reaction products depend on the temperature and the ratio $CaO/Al_2O_3 + SiO_2$ in the zeolite/lime mixtures. When the ratio was 0.8, calcium silicate hydrate and a tobermorite phase with a characteristic 11-angstrom lattice spacing

formed at 90° C. At higher temperatures (170 and 280° C), only tobermorite formed. At higher temperatures and higher $CaO/Al_2O_3 + SiO_2$ ratios, more crystalline tobermorites and hydrogarnets were formed. Zeolitic gels forming from high calcium glasses can easily produce both tobermorites and zeolites observed in hardened binders. Much of the variation in products observed during the formation of hardened binders using silica- and alumina-rich solids and alkali solutions probably relates to the composition of the materials used as reactants and the temperature of the reaction. For example, many waste silicate glasses or slags used in binders contain relatively small amounts of aluminum, and although some high silica zeolites can form, aluminum is a necessary structural component in most zeolite minerals. The problem of zeolite formation may also be related to the high calcium content of the waste glasses commonly used in alkali-activated slag. A high calcium content also favors the formation of tobermorites over zeolites.

15. Slags have been the most widely used raw material for the production of alkali-activated binders, but in the 1970's and 1980's, other fine-grained alumino-silicates were employed. Clays (both natural and fired) and industrial ash and dust were shown to be potential reactive materials. In 1976 and 1977, Davidovits obtained patents covering the use of alumino-silicate binders to form structural materials by applying heat and pressure to an alkaline mixture of clay and silica (Davidovits 1976, 1979; Davidovits and Legrand 1977). These products were, in some cases, similar to experimentally produced zeolites.

16. Dr. Bengt Forss obtained patents in 1981 on a binder formed from an alkaline mixture of pozzolanic materials (granulated slags and fly ash). The Forss patent (Forss 1981) outlined the use of a mixture of caustic (NaOH) and alkali salts (especially silicates and carbonates) with a mixture of metallurgical slag and cement clinker and/or fly ash.

17. Minerals formed by reacting bases with sources of alumina and silica are unusual in that they not only are hard structural binders, but some of the crystalline products (especially the zeolites) are also valuable as catalysts (reaction promoters) or separation systems (molecular sieves). Interest generated in the chemical and petroleum industries has led to the extensive investigations into alkali/alumino-silicate reactions (Breck 1974; Barrer 1982). While these investigations have been directed toward producing specific crystal structures from specific starting materials, they have

demonstrated the versatile nature of the alkaline reactions and have assisted in developing an understanding of low-temperature alumino-silicate chemistry. Zeolite synthesis has shown that many bases other than sodium or potassium hydroxide can be used in silicate reactions. A wide range of low-cost materials containing silicon and aluminum can be used as a starting material (ash, slag, clay, volcanic rock). Relatively small amounts of some organic compounds can be used if necessary to direct the formation of specific crystal structures. For example, some silica/alumina compounds (cancrinites) will not crystallize unless a template compound (sodium sulfate or nitrate) is present in solution to fill the crystal openings (Barrer 1982).

18. The research into catalysts and molecular sieves indicates that a broad family of alumino-silicate materials with a wide range of properties exist. For example, many of the zeolitic compounds have excellent stability at high temperatures, far better than constituents in conventional portland cement binders. The silica-rich zeolites (like clinoptilolite) remain intact when leached with strong mineral acids, indicating a potential for better chemical durability than conventional portland cement binders.

19. Alkali-alumino-silicate reactions have also been used in waste disposal. The compounds that form in low-temperature clay-alkali reactions (zeolites and cancrinites) are large cage-like crystals that can sequester molecules of waste material. Caustic radioactive wastes can be reacted with clays such as bentonite, kaolinite, halloysite and dickite. When reacted in the proper proportion, the clay-alkali-waste mixture becomes a durable monolithic solid (Barney 1974, 1975; Thompson 1975, 1976). Research with simulated waste solutions demonstrated that in many clay-alkali reactions, inorganic salts in solution (sulphates, nitrates or molybdates) were necessary to promote the formation of specific crystal structures. The soluble salts fill the cage-like intracrystalline pores and become a mandrel around which the alumina/silica cage forms, but these "caged" molecules are not specifically part of the crystal structure.

20. Alkali-activation of a variety of glassy slags to produce binders has been studied for over forty years. Within the last decade, research has expanded into other raw materials (ash, furnace dust, and clay). The increasing fuel costs involved in conventional cement production and the increasing availability of fine-grained alumino-silicate dusts from air pollution control equipment make alkali-activated alumino-silicate binders economically attractive.

Binder Materials

21. Alkali-activated binders can be prepared with a wide variety of natural materials or waste with a minimum amount of processing. A variety of alkaline materials can be used to promote binder formation. Accessory components can be used to direct or promote crystallization. Table 1 summarizes some of the potential sources for components used in alkali-activated binders.

22. In developing binders, the costs of materials are often critical. Efforts are directed toward finding the least expensive blend of materials that will produce high strength cementation. The usual approach has involved screening waste products or naturally occurring silica and/or alumina-rich materials to determine which will produce cementing reactions when mixed with strong alkalis. Four different classes of alkali additives are recognized (Boldyrev and Tumenez 1984):

Group I	Sodium or potassium hydroxides or mixed fused alkalis.
Group II	Non-silicate salts of sodium or potassium such as sodium carbonate, potassium carbonate, sodium fluoride and others.
Group III	Silicate salts of alkali metals, such as sodium or potassium ortho- or metasilicates.
Group IV	Alumino-silicate or aluminate salts such as sodium or potassium aluminates.

Reactions of alkali with silica/alumina sources may require heating. The most consistently reactive and cementing solid phases are materials with more than 95 percent glassy (or noncrystalline) constituents. The chemical composition of the glassy solid should be such that the ratio

$$\frac{CaO + CaS + 1/2\ MgO + Al_2O_3}{SiO_2 + MnO} > 1.9$$

(Forss, 1981). Where metallurgical slags are screened, slag with a CaO/SiO_2 ratio between 1.1 and 1.3 are considered useable. In some processes slag is blended with pumice, fly ash, or other pozzolans and lime to adjust the CaO/SiO_2 ratio. For example, the solid component of a binder could consist of 75 percent slag and 25 percent basalt, or 50 percent slag and 25 percent clay and 25 percent cement kiln dust (Boldyrev and Tumenez 1984).

23. Many of the potentially useful silica/alumina-rich solids are

Table 1

Sources for Binder Components

Sources of Silica and/or Alumina	Sources of Alkali	Sources of Crystallization Modifiers
	Alkali metal hydroxide	Salts
	Alkali earth hydroxides	sulfates
Volcanic pumice	and oxides	carbonate
Volcanic trass	Salts (fluorides,	chlorides
Fine-grained effusive rock	halides, carbonates,	chlorates
perlite	phosphates, sulfates,	fluorides
liparite	and others)	Organics
andesite		tetramethyl-
basalt	Organic bases	ammonium
	(ammonium hydroxide	dyes
Fly ash	esp. quaternary	
Cement kiln dust	bases)	
Lime kiln dust		
Silica fume	Silicates and	
	aluminates	
Metallurgical slag		
titaniferous		
ferromanganese		
nickel-iron		
cupola		
open hearth		
electrothermophosphoric		
Portland cement clinker		
Clay (fired clays)		
kaolinite		
illite		
montmorillonite		
Mineral-rich ash		

available as glassy, fine-grained wastes that do not require grinding. For example, fly ash and kiln dust are produced as waste in electrostatic precipitators or bag house filters. Other raw materials include glassy wastes from metal refining (blast furnace slags, copper retort slags). Slags typically are quenched to assure that they contain a high proportion of glass and are ground in a ball mill or rod mill. Wastes can be blended to adjust the CaO/SiO_2 ratio or where calcium levels are low, lime is added directly to the blended solids; it is not necessary to fuse the calcium into a glassy mass.

24. Alkali additives needed for binders can also be obtained from wastes. Concentrated alkali wastes are produced in synthetic fiber production, in treating of natural fibers, and in the manufacture of dyes and pigments. Where alkali wastes (sodium or potassium hydroxide) are not available, sodium or potassium salts can be mixed with alkali-earth hydroxides (for example, lime) to form hydroxides of alkali metals. The most useful alkali salts are generally the least soluble; for example, sodium carbonate is a better activator component than sodium chloride.

25. All the components in an alkali-activated alumino-silicate binder can be wastes. Major economic factors in developing binders for marketing are related to sources of suitable waste material and with costs of transportation. Binders do not require direct production from a kiln. Major capital investments are called for only in drying, grinding, air classifying and storing and blending binder components (Forss 1981).

Processing Binder Materials

Alumino-silicate base material

26. Solid phases in alkali-activated binders differ from conventional portland cement in that the finer the grain-size of the solid phases, the better the ultimate strength gain. Solids cannot be overground. Fine-grinding presents large areas for liquid-solid interaction and gel formation. Generally, the more crystalline and less reactive the component, the finer the material must be ground to be useful. Glassy slags are ground to 3,000 to 3,800 cm^2/g (Blaine), while more crystalline components, like rock may have to be ground to 4,000 or 5,000 cm^2/g. Grinding is normally done in conventional rod mills or ball mills.

27. Where solids of different hardnesses (such as slag and portland

cement clinker) are to be blended, they are generally not ground together. However, some plasticizers (such as alkali lignosulphonate) have a favorable effect on grinding and some retarding compounds such as sodium gluconate or sodium bicaonate are added during grinding to assure the reagents are distributed uniformly through the mix. Difficulties associated with grinding can be reduced by using the maximum amount of fine-grained, air-classified particulates such as fly ash or kiln dust.

28. Granulated slag would typically be ground to have a surface area of 3,000-4,000 cm^2/g, but Metso and Kajaus (1983) demonstrated that pelletized slag with a surface of approximately 3,400 cm^2/g could be employed without a loss in strength compared to powdered slag. Where fresh ground slag could undergo a cementing reaction when water alone was added, this self-cementing property could be preserved longer if the ground slag was pelletized. Pelletizing the alumino-silicate solid may reduce dust problems without decreasing the reactivity of the solid with alkali.

29. The chemical composition of the glasses or disordered silica/alumina compounds used in the solid phase of the binder has proved to be relatively unimportant if the solids are largely (> 95 percent) noncrystalline or glassy. The major specification for the chemical composition of slag is that the CaO/SiO_2 ratio should be between 1.0 and 1.3 (Forss 1981). Trace constituents are not considered important.

Alkali activators

30. The alkali-activator or activators can be added as a liquid or as a solid ground into the glassy or noncrystalline alumino-silicate. Solid sodium hydroxide or sodium carbonate can be ground into the alumino-silicate mixture to provide a one-component binder that is mixed with water. The only problems encountered in intermixing the activator has risen from the difficulty in maintaining the very active reagents during storage. Sodium hydroxide absorbs moisture from the air and reacts with carbon dioxide in the air to form sodium carbonate. Carbonation and moisture problems can be minimized by using calcium hydroxide and a sodium salt (usually sodium carbonate) to generate the required amount of sodium hydroxide when water is added to the mix (Purdon 1940). Calcium hydroxide will also react with carbon dioxide and form calcium carbonate, a less reactive compound. An alternative activator is sodium silicate. The silicate can be adoed as a liquid or as dry, solid sodium metasilicate hydrate (Voinovitch, Raverdy and Dron 1980).

31. Activators may also contain wetting agents (plasticizers) to reduce the amount of water needed and to assist in mixing. Lignosulphonates, or sulphonated lignins, have proven to be more effective than melamine or naphthalene-based superplasticizers (Forss 1981, 1982). Lignosulphonates can cause excessive air entrainment and because most alkali-activated binders are poured as densely as possible, anti-foaming agents are needed. Antifoaming agents, such as tributyl phosphate, can be added to the activator solution to produce more compact mixes. Sodium bicarbonate has also been used to increase the fluidity of the mix without adding air. The activation mixture may also contain compounds added to regulate set times. Potentially useful regulators include sodium gluconate, sodium sulfate, and sodium bicarbonate (Forss 1981).

32. Liquid activators offer significant advantages over solids interground with the alumino-silicate particulates. The liquid can be sealed up out of contact with air to insure the activators do not carbonate. Uniform distribution of plasticizers, retarders and air-controlling agents is easier to achieve in the liquid than in the solid additive.

33. Some experimental activation mixtures used with glassy slags contain gypsum or phosphogypsum (Voinovitch, Raverdy and Dron 1980; Metso and Kajaus 1983). Adding sulfate changes the sequence of setting reactions that can occur. Complex calcium sulfoaluminates (such as ettringite) form through reactions between gypsum and the aluminum in the slags. Calcium sulfoaluminates hydrates exist in several forms and transitions from one hydrate to another can produce dimensional changes and swelling or cracking. Exposed surfaces of cemented material containing sulfoaluminates can deteriorate through reactions with carbon dioxide (D'Ans and Eick 1954). Gypsum is generally not added to alkali activation mixtures that are proposed for commercial application.

Aggregates or fillers

34. Alkali-activated binders can be employed successfully with a wide variety of filler materials, many of which would not be classed a quality aggregate (for portland cement concrete). Aggregates with high clay content (up to 8 percent), or high dust content (up to 20 percent), even ore tailings, or soils such as sandy loam or sandy clay have been employed as fillers without sacrificing the high early strength characteristic of alkali-activated binders (Boldyrev and Tumenez 1984). When soils are used as fillers, the products are referred to as soil-silicate concretes. The strengths obtained

with soil/binder mixtures vary widely depending on the composition of the binder and soil and the curing technique. Glukhovskii et al. (1967) reported maximum strengths of 1,780 kgf/cm^2 (25,300 psi or 174 MPa) from autoclave-curing a mixture of approximately 40 percent metallurgical slag, and 60 percent sandy loam with 3 percent sodium hydroxide. Fine-grained alumina or silica-rich components, such as clay or silica flour present in the filler react with the strong alkali mixture and are gelatinized, thus becoming part of the binder. The activator prevents fines from interfering with bonding.

35. Alkali-activated binders have been used with fine aggregate contaminated with salt. Forss (1983) reported that in testing done at Abu Dhabi in 1980, all of the 0-8 mm gravel in a mix was replaced with 0-2 mm dune sand without detrimental effects. Although the alkali binder contains a variety of primarily sodium or potassium salts, aggregates that contain reactive SiO_2 (opaline rock) undergo much less expansion than that observed with ordinary portland cement binders. The low expansion is thought to be due to absence of free calcium hydroxide in the binder. Tests with alkali-activated mixes where opaline aggregate was used showed lower reaction rates than portland cement concretes. Metso (1982) blended up to 15 percent reactive opaline sand into a alkali-activated binder prepared with Finnish slag. The slag had to be blended with 3.9 percent sodium (as NaOH) to produce a reaction product. No reactions were observed with activation additions below 3.9 percent sodium; this amount of activator is 2.5 times the amount needed to produce cementation. No problems with opaline reaction with aggregate should occur in alkali-activated mixes unless alkali activator is added far in excess of the amount needed to produce a well-cemented slag.

36. While it is best practice to use the most competent and compatible aggregate available, both conventional quality and substandard aggregates are useable. Boldyrev and Tumenez (1984) point out that alkali-activated alumino-silicate binders are particularly useful in Siberia and Central Asia where high quality aggregates are rare.

Mixing Binder and Filler Components

37. Alkali-activated alumino-silicate mixes are typically made up with a low water-to-solid binder ratio (0.2), approximately 30 percent lower than portland cement. The mix goes from stiff to medium with a small amount of

additional water. Large pilings have been cast without vibration using a water-to-solid ratio of 0.27-0.28. Low water content mixes are relatively sticky, but flow well under vibration. Mixing is most efficiently done using a pan mixer or a plow mixer rather than a drum mixer. Only the more fluid mixes can be handled with a drum mixer (Forss 1983).

38. During mixing, the liquid alkali and slag dampen slowly and become wet and fluid only after 8-25 minutes of reaction. Investigations conducted using nuclear magnetic resonance to track the amounts of bound and unbound water show that the reacting mixture first goes through a phase where the alkali attacks the silica and forms gels. As a more crystalline (condensed) structures form from the gel, excess water is expelled and the mixture becomes more fluid or undergoes liquefaction. As the hardening proceeds a crystalline hydrate forms and more of the water becomes bound into crystal matrices (Grankovskii, et al. 1982; Royak, et al. 1974; Kudryavtsev, et al. 1977).

39. The alkali added to the binder is corrosive to most metals. Alkali-activated binders have pH's ranging from 12-14. The high pH does not corrode steel mixing equipment if adequate care is taken, but aluminum and magnesium metal corrode quickly. Only steel equipment should be used in mixing, pumping or finishing the hardening mixture.

40. Alkali-activated binders and aggregates should always be mixed in clean equipment. Hardened binder can cause rapid setting of freshly mixed material because the solid binder furnishes nuclei for the crystallization of the silicate gels.

41. If alkali-activated binder is mixed with fresh (wet) portland cement, the alkali-activated binder stiffens quickly (Kukko 1980). Where the same mixers are used for alkali-activated binder and ordinary portland cement, care must be taken to clean the mixers carefully between batches.

Placing and Curing of Binder/Filler Mixtures

42. Alkali-activated binder/filler mixtures are prepared with a low water content, and the mixes do not undergo the usual hydration reactions observed in portland cement concrete (Forss 1982). The fluidity of alkali-activated mixes changes rapidly as water is added and fluidity changes as mixing progresses (Royak, et al. 1974; Kudryavtsev, et al. 1977). The mixes

tend to remain fluid longer if they are worked continuously. Typical working times without retarders are 30 to 45 minutes.

43. When low-slump, low water-to-solid mixes are used, vibration can greatly improve placement of the mix. Glukhovskii, et al. (1967) cite examples of casting operations where vibration frequencies of 3000 to 6000 oscillations/minute were combined with pressures up to 8.2 kPa (1.2 psi). Vibration during placement is done in the same way portland cement concrete is vibrated, using rods or table vibrators.

44. The heat of hydration of alkali-activated binders is generally less than half that of portland cement. Without thermal curing, the strength gain in the alkali-activated binder occurs at approximately the same rate as in portland cement hydrate. Rapid gains in early strength are noted when the binder/filler mix is moist-heat cured at approximately 50° C (122° F). Maturity is generally measured as hours x ° C. In typical alkali-activated systems, 500 hr ° C is considered mature or cured material (Forss 1983).

45. Alkali-activated binder/filler mixtures can be heat-cured immediately after pouring; but prestoring for up to one hour is useful in obtaining high strengths. Glukhovskii, et al. (1967) specifies a two to five hour prestoring period, steaming for six hours and curing at 90° C for an additional three hours. Experimental work reported by Grankovskii, et al. (1982) indicated that heat curing beyond three hours did little to increase the strength.

46. Dry heat curing even at temperatures as low as 60° C can result in lower strengths (Kutti, et al. 1982; Talling 1985). The lower strengths are probably due to the incomplete reaction of the binder caused by the drying of the specimens.

47. Autoclave curing results in very high early strengths, up to 55 MPa (8000 psi) compressive strength in one hour. Autoclave procedures used with alkali-activated binders have followed techniques used for portland cement products (180° C, 0.9 MPa steam pressure for eight hours). The major difference between autoclaved portland cement hydrate and autoclaved alkali-activated binder, is that the alkali-activated products gain strength faster (Kutti, et al. 1982).

Summary of Properties of Cured Material

48. Alkali-activated alumino-silicate binders offer some unique

properties when compared to other binders such as Type I portland cement. When heat cured, alkali-activated binders reach very high strength rapidly and have remarkable ultimate strengths and high durability. Alkali-activated binder mixes can be made very dense (2.5 kg/liter for wet mix). The high density and reduced porosity can decrease shrinkage and increase frost resistance. Alkali-activated binders do not normally contain lime or aluminum compounds that can react with sulfate; therefore, they are sulfate resistant. Although the pH of hardened alkali-activated binders can be very high (pH 12-14), the density of the binder usually prevents any corrosive effects on reinforcing steel.

High strength

49. Strength developed in most binder mixes is related to the amount of binder used, the ratio of water to binder, and the temperatures used for hardening and curing. With comparable mixes, an alkali-activated binder can reach 28-day compressive strengths that are 20-40 percent higher than Type I portland cement concrete (Kukko 1980). Moderate heating causes a rapid increase in strength gain. With mixing at 20° C and curing at 40° C, for example, an alkali-activated slag binder is reported to reach over 50 MPa (7250 psi) unconfined compressive strength in less than one day. The flexural strength of alkali-activated binders/aggregate mixes is approximately the same as Type I portland cement concrete; 1/7 to 1/10 of the compressive strength.

Shrinkage

50. The low water-to-solid ratio and low porosity results in lower shrinkage in hardened alkali-activated slag binders when compared to Type I Portland cement concrete when mixes of similar workability and strength are compared (Kukko 1980; Forss 1982).

Creep

51. Creep, the increased strain under sustained stress, is approximately the same in alkali-activated binders/aggregate mixes and in Type I portland cement concrete (Kukko 1980). Glukhovskii, et al. (1967) indicated that substitution of soil for aggregate can cause high rates of creep to appear in alkali-activated slag mixes.

Thermal properties

52. The coefficient of linear expansion of alkali-activated binder/aggregate mixes is within the order of that observed for Type I portland cement concrete containing a comparable amount of binding agent. For both

materials, the coefficient is 0.9-1.3 x 10^{-5}/°C. When alkali-activated binder/aggregate mixes and ordinary portland cement concrete are made with similar aggregate, their fire resistance is similar; both show significant loss of strength (20 percent or more decrease) above 300° C (Kukko 1980). Alkali-activated binders can be prepared with selected raw material but similar binder chemistry and be stable up to 1,150° C (Davidovits 1983).

Freeze-thaw resistance

53. Alkali-activated binder aggregate mixes, although not air-entrained, are comparable to (Kukko 1980; Forss 1982) or better than (Glukhovskii 1974) portland cement concrete in resistance to freeze-thaw deterioration.

Sulfate resistance

54. Alkali-activated binder/aggregate mixes are made with slag and contain no free lime or reactive aluminum compounds that can reduce strength in ordinary portland cement concrete that is exposed to sulfate. Alkali-activated mixes exceed even sulfate resistant portland cement concrete in their durability and are generally unaffected by sulfate (Kukko 1980, Boldyrev and Tumenez 1984).

Corrosion resistance

55. Alkali-activated binders are very dense and, although the pH in the mix is high, no deterioration in reinforcing steel was noted in one year duration testing (Kukko 1980).

PART III: POTENTIAL MILITARY APPLICATIONS

Statement of Problem

56. A fundamental problem confronting the Army yesterday, today, and tomorrow is the effective movement of weapon systems, men, and supplies over the ground; i.e., land mobility. The ability to move as well as use fire power and communicate are critical to winning the battle.

57. An analysis of the Army's Combat Service Support Mission Area has identified a need for a new, improved general engineering capability to increase the mobility and efficiency of field units. There is a need to provide rapid construction and rehabilitation. of lines of communication and logistics facilities in the Theater of Operations (TO). Emphasis needs to be placed on new methods and materials which are faster and more efficient using less labor, and fewer imported construction materials. The capability to provide responsive engineer support to rapidly deployed forces in nontraditional environments must be enhanced.

58. To meet the above needs, the Army is developing new and innovative concepts for constructing and repairing ports, roads, airfields, and storage areas in the TO. The search for binding agents for paving and/or structural materials to aid in this development is an unending one. Some desirable material characteristics are as follows:

- a. Easily mixed and placed.
- b. Fast setting.
- c. Ultra-early strength.
- d. Ultra-high strength
  - (1) High compressive strength.
  - (2) High flexural strength.
- e. Strong bonding to rebar.
- f. Strong bonding to existing surfaces.
- g. Use of a wide variety of aggregates without strength loss.
- h. Durability to trafficking.
- i. Resistance to sulfate attack.
- j. Resistance to heat.
- k. Resistance to chemical attack.

l. High moldability

m. Simple storage.

59. The Army Corps of Engineers Long-Range Science and Technology Plan sets forth the studies aimed at aiding the Army in meeting its Combat Service Support Mission Area Deficiencies. Objectives of selected studies are briefly described below. In every instance, a material having some of the previously mentioned desired characteristics could significantly impact the attainment of these objectives.

Lines of communication (repair)

60. Lines-of-communications (repair) objectives include the following:

a. Repair and Restoration of Paved Surfaces. To develop an improved rapid runway repair system that will be suitable for all climatic conditions, reduce manpower requirements, reduce total repair time, and improve the permanency of the repair.

b. Evaluation and Repair of War-Damaged Port Facilities. To develop an improved capability to evaluate and repair critically needed war-damaged port facilities to include evaluating materials and systems to be used.

c. Repair of Threat-Damaged Roads and Railroads. To provide field units with repair techniques for roads and railroads using, where possible, locally available materials.

d. Development of Air Transportable Road/Airfield Repair Kit. To develop an airmobile airfield repair kit to allow 40 passes of a cargo aircraft. The kit could also be used to repair roads.

e. Quick Rehabilitation Techniques for Roads and Airfields. To develop design criteria with reliability factors for the quick rehabilitation of roads and airfields.

Lines of communication (construction)

61. Lines-of-communication (construction) objectives include:

a. Use of Alternate Materials and Relaxed Criteria for Pavement Construction. To investigate possibilities of relaxation of pavement and paving material standards due to constraints of time and availability of quality materials.

b. Methods for Road and Airfield Construction in Adverse Environments. To develop or modify criteria and construction practice and to identify material requirements so that road and airfield construction can be performed in adverse environmental conditions such as extreme dry, arid regions or during periods of intense rainfall.

c. Alternate Binder Evaluation for Surfacing. To establish the state of knowledge on alternate binders and generate a data base to evaluate their potential as a pavement binder.

Logistics over the shore (LOTS)

62. Logistics-over-the-shore objectives are as follows:

a. Design and Construction Criteria for Large Storage Areas for LOTS. To determine the available ways of constructing large storage areas using several different materials and surfacings and to develop design and construction criteria for the most promising types.

b. Investigations of Fabrics for Horizontal Reinforcement of Sand. To develop design criteria for horizontal reinforcement of sand, using fabrics, and specifically determine minimum fabric properties required, optimum placement depth, anchor concepts, and surfacing treatments for rapid construction techniques in moving and storing supply cargo over loose sand areas.

c. Rapid Stabilization of Sands with Emulsions. To develop and evaluate techniques for rapidly stabilizing sands with emulsions to produce road, helipad, and storage area support layers in beach and desert type sands.

d. Surfacing for Container Storage Areas. To develop an expedient surfacing material for the LOTS environment which will support military vehicle traffic normally required to operate across a sand beach.

e. Design of Prefabricated Expedient Surfacing for Use with Sand-Grid Concept. To design a reliable expedient surfacing system for use as a vehicle wearing surface for the sand-grid beach stabilization concept.

f. Access/Egress System for Improved Mobility in Soft Soils. To develop techniques for rapid construction and use of materials that provide trafficable access/egress routes over extremely soft soils generally found in conjunction with wet gaps.

Application Areas and Material Requirements

Repairs

63. Repairs to lines of communication facilities such as rigid pavement runways and roads in the TO will be made in an expedient manner using material on hand and whatever equipment and personnel are available. The major consideration will be the restoration of traffic with a minimum delay. Current planning calls for fast-setting portland cement binders and/or organic polymers and the maximum amount of prefabricated materials possible. Any binder employed for expedient repair must be stable under a wide variety storage condition for an extended period of time. Specialized mixing equipment should not be required. Aggregate used for repair will often be rubble from earlier concrete structures and thus bonding to aggregate that has not been screened

or washed may be required. No selection of aggregate will be possible, therefore the ability to form a solid monolithic material with a wide variety of wet or dry fillers will be required. Fast setting and high-early strength are critical; the characteristics of the material in finishing operations are not important beyond producing a trafficKable surface. Binders that can be mixed and placed without evolving fumes or generating heat offer distinct advantages in that they require lower levels of protection for personnel.

Construction

64. Paving used in construction of lines of communication facilities in the TO will vary widely depending on the circumstances and the available material. The normal rigid pavement binder would be conventional or rapid-set portland cement. Any alternate binder employed would have to exhibit higher earlier and higher ultimate strength so that construction time can be saved through reduced subgrade preparation and/or structural reinforcement. Fast-setting is needed to facilitate early trafficking. The ability of a binder to develop high-strength pavement using a wide variety of substandard aggregates during construction in adverse climatic conditions is also desirable.

Logistics over the shore (LOTS)

65. Pavement construction in a LOTS operation offers significant engineering challenges. The containerization of Army cargo for seaborne delivery is progressing. In an envisioned LOTS operation, truck-semitrailers will move a large number of supply containers weighing up to 20 tons each between shipside and large temporary storage yards within a distance of approximately 6 km. Roads and hardstands will be required to support the heavy loads in the beach environment. It is desirable to haul in the minimum amount of construction material making use of what is locally available. The binder should be able to accept local aggregate (preferably sand which is salt contaminated) as a filler. The ability to use low-grade mix water such as sea water or brine is also desirable. Finally, a fast setting mix that produces high early strength is needed to allow fast, high-load trafficking.

PART IV: PROPERTIES AND USES OF A COMMERCIALLY DEVELOPED ALKALI-ACTIVATED PRODUCT IN MILITARY OPERATIONS

66. The following data were prepared under contract by Pyrament N. V. to provide an example of the potential performance that can be expected from alkali-activated alumino-silicate binder in meeting specific military needs. The data presented were developed by the contractor during their research and development operations. The mention of a specific product does not constitute a recommendation or endorsement of any kind by any government department or agency.

Product Development

67. Lone Star Industries, the largest American manufacturer and supplier of cement, has been involved in research and development for many years. The most recent development of these research efforts is PYRAMENT^{TM} blended cement which is based on an alumino-silicate binding system. Additionally, a related family of alumino-silicate binders has been developed which will have widely varying uses.

68. Lone Star has formed a new subsidiary corporation based on this discovery - PYRAMENT N. V., which has been entrusted with the development of PYRAMENT^{TM} and its related derivatives. PYRAMENT^{TM} is the brand name of a patented binder with properties and characteristics that differ from those of portland cement. The formulations now available from Pyrament N. V. have been developed from the patents of a French chemist, Dr. Joseph Davidovits (Davidovits 1976; Davidovits and LeGrand 1977). These original worldwide patent rights are owned by Pyrament N. V., and Dr. Davidovits has been retained to help with the development. Pyrament N. V. now has a number of economically viable binder formulations which can be used in various ways to solve long standing problems.

69. The manufacture of PYRAMENT^{TM} binder involves the processing and selection of raw materials which are unlike that of portland cement. In addition to the chemical and mechanical advantages, Pyrament^{TM} binders can be manufactured with an energy savings of at least 70 percent over that of portland cement and is almost completely free of the air pollution problems associated with the manufacture of portland cement.

Summary of Properties

70. The technology of PYRAMENT^{TM} blended cement brings together a number of different advancements in binder technology which have been researched throughout the past decades. Portland cement hydration, pozzolanic activity, alkali activation, and alumino-silicate binder mechanisms, have been combined in one formulation. PYRAMENT^{TM} binder/aggregate blends show impressive early strengths as well as very high ultimate strengths (Figure 2). Minimal volume change makes the material highly resistant to shrinkage cracking (Figure 3). PYRAMENT^{TM} binders show a high degree of sulfate resistance (Figure 4) and retain significant strength at elevated temperatures (Figure 5). PYRAMENT^{TM} formulations can be used as blended cements in the preparation of mortar and concrete, but the advantages do not end at this level. In addition, other PYRAMENT^{TM} formulations make possible a number of products, the manufacture of which has been principally restricted to metals, plastics and kiln-fired clays.

Handling Characteristics

71. PYRAMENT^{TM} binder/aggregate blends can be formulated having a useable slump range from 0 to 12 cm, depending upon the user's needs. Mixing and placing is done with conventional equipment (Figures 6 and 7). As with portland cement and other blended cements, the curing of PYRAMENT^{TM} concretes can be achieved either at ambient temperatures or with steam equipment which can be inexpensively obtained and operated. Steam curing or other means of obtaining elevated temperatures, makes greatly accelerated curing times possible.

Application to Problem Situations

Rapid repair and restoration

72. When using PYRAMENT^{TM} binders--properly placed and cured--repaired areas can be returned to use within four hours. Repeated vehicle trafficking over an area which has been repaired using PYRAMENT^{TM} materials, should show it to be as effective in four hours as portland cement after 28 days of curing. Early, high strength gain now underscores the potential of making

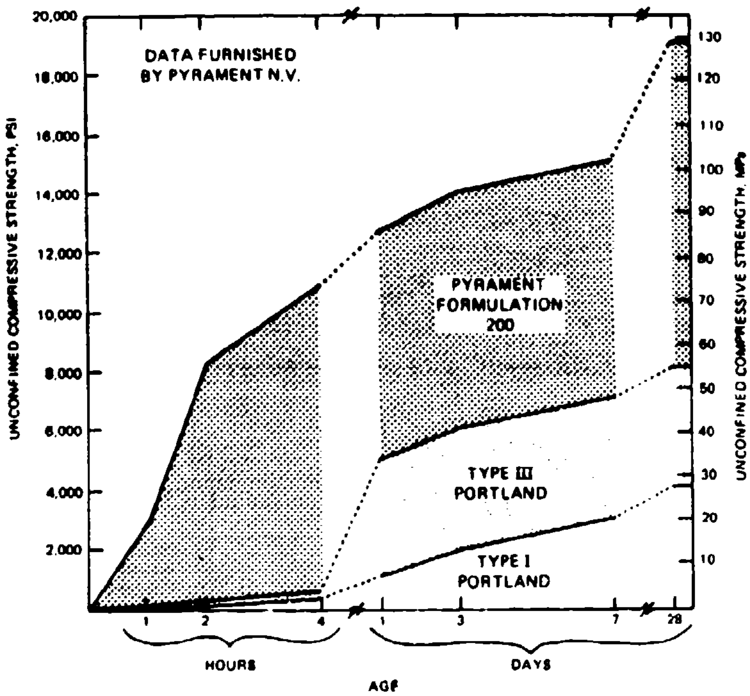

Figure 2. Strength gain for binder/aggregate mixes

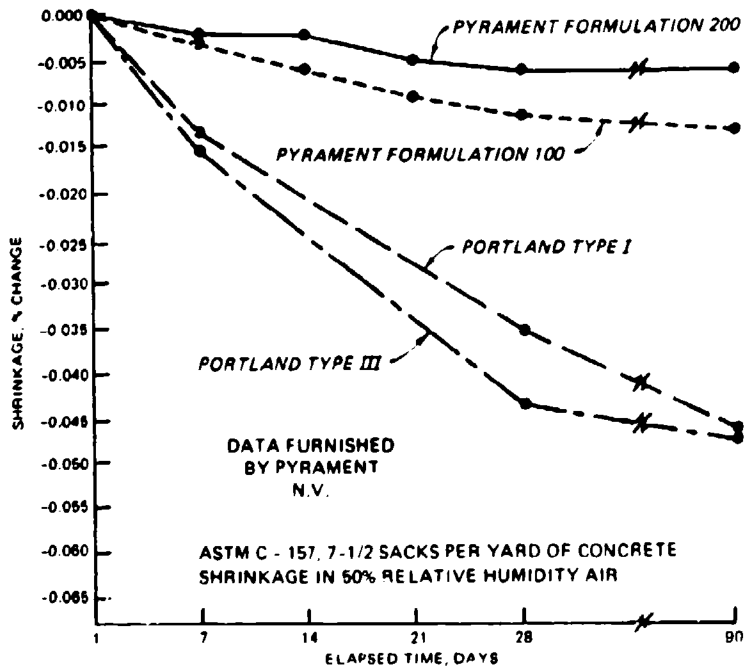

Figure 3. Shrinkage observed in binder/aggregate mixes

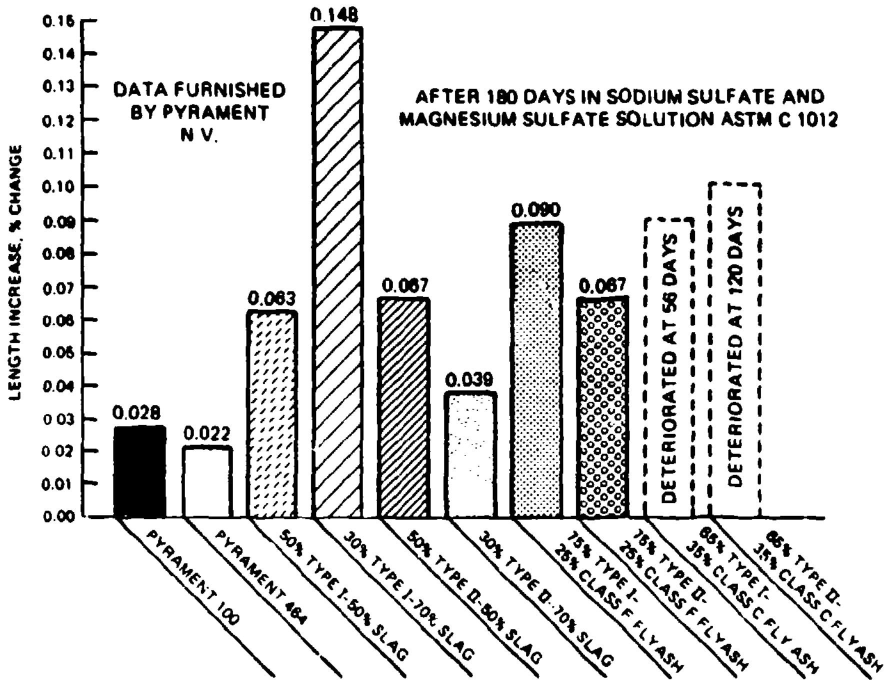

Figure 4. Relative sulfate resistance for binder/aggregate mixes

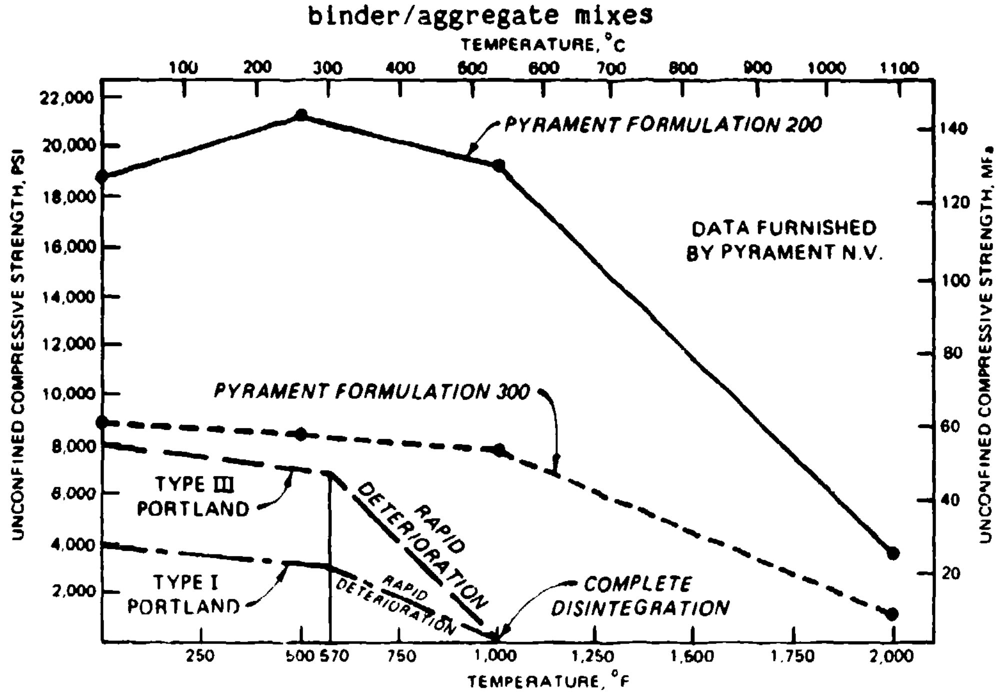

Figure 5. Strength retention at elevated temperatures for binder/aggregate mixes

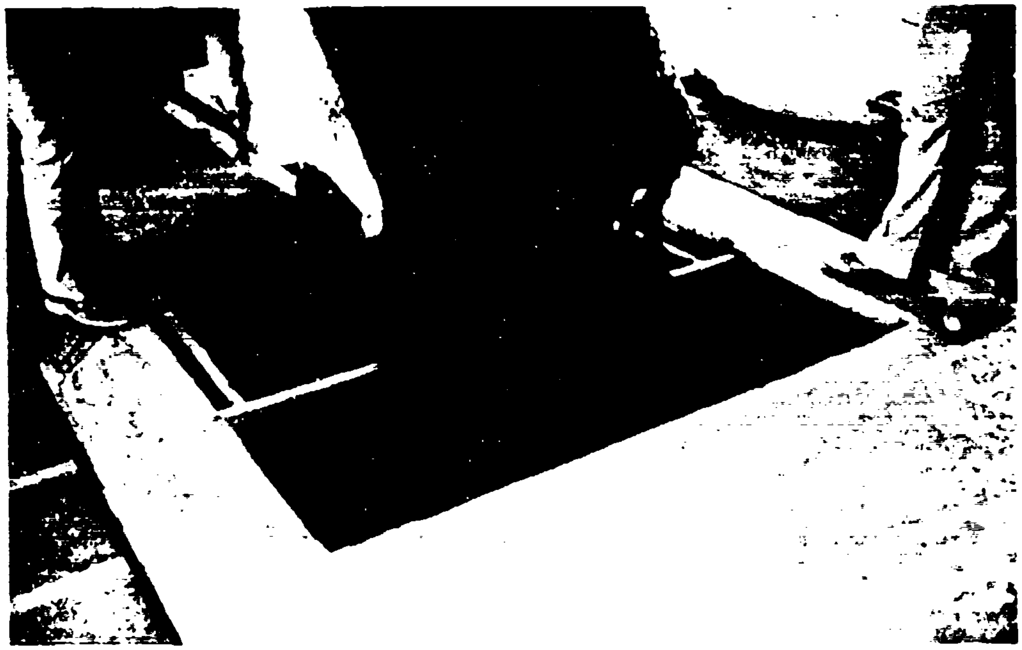

Figure 6. Placing PYRAMENT^{TM} concrete using a skip bucket and wooden formwork

Figure 7. Working and screeding the patch material

permanent rapid repairs of the quality and durability heretofore considered unobtainable.

73. Properties such as these point to the obvious body of patching repair situations where such benefits would be of prime concern. Early high compressive and flexural strengths allow loading to take place within a time frame previously thought unobtainable without resorting to highly expensive materials. Volume stability allows PYRAMENT™ binders to maintain a good bond to surrounding surfaces without pulling away because of mass reduction due to shrinkage.

74. Where immediate return to service is critical, such as for threat-damaged roads, railroads and port facilities, the expedient nature of PYRAMENT™ compounds facilitate the rehabilitation of these areas with conventional equipment and manpower. Turbines, or other large machinery that must be anchored with grout, can be put back into operation much sooner, thus saving expensive down-time.

75. Expedient repairs and restorations can be made on bridges and roadways because the overlay and paving techniques can now be accelerated. Although the construction methods will be comparable to that of portland cement, the time of cure and return to service can be significantly shortened. In April 1985, a test was performed at US Army Corps of Engineers Waterways Experiment Station simulating repair of damaged pavement. Repairs to pavement breaks were made using PYRAMENT™ blended cement concrete. Details of the trial patches are presented in Part V.

Rapid construction

76. PYRAMENT™ binders are manufactured in a different manner than that of portland cement. It does not require extreme high temperature kilns, with large expenditures of fuel, nor does it require such a large capital investment in plant and equipment. Additionally, research work on PYRAMENT™ binder formulations has exemplified the possibility of manufacturing binders of the alumino-silicate variety wherever the necessary raw materials exist. The research work has uncovered the possibility of manufacturing lower quality but acceptable binders where alternate sources are available.

77. The performance of PYRAMENT™ binders may actually be enhanced by some extreme weather conditions such as hot, dry deserts. These weather conditions may facilitate the rapid curing of placed concrete. Also, low water requirements and the property of not needing lengthy moist curing would be

helpful under these conditions. Low temperatures would not be a problem since heat is required anyway for rapid curing; therefore, the same process could be used under all temperature conditions.

78. Extruded products, continuous slip form products, and automated precast products will be impacted favorably by the availability of PYRAMENT^{TM} materials and their rapid curing advantages. This will result in not only a reduction of time but also a reduction of cost for construction.

Logistics problems

79. The research work involving PYRAMENT^{TM} formulations is ongoing. Possibilities exist for using variable quality aggregates as well as salt or contaminated mix water. Each of these problems may be solved favorably and may point to our ability to have an available construction material without transporting aggregate and mix water long distances. Ability to use local materials in the manufacture of a binder suitable for the Army's needs has long been an objective.

80. It is envisioned that aggregate varieties, from low-quality, soft aggregates to well-graded quartz, can be used with PYRAMENT^{TM} binders. Since PYRAMENT^{TM} binders bond well to existing portland cement concrete structures, broken concrete may be used as aggregate. A new binder system may improve the ability of the military to solve some of its logistical problems. The development of binders such as PYRAMENT^{TM} indicates that the solution may be in sight.

PART V: PAVEMENT REPAIR DEMONSTRATION

81. Pyrament N. V. presented a demonstration of a new alumino-silicate binder at WES on 9-12 April, 1985. The demonstration consisted of producing a small pavement patches and testing cylinders of hardened binder and aggregate.

82. Personnel from Pyrament N. V. arrived at WES and set up equipment on 9 April. To check out the equipment, a small 0.9 m x 1.5 m (3 ft x 5 ft) slab, 9 cm thick (3 1/2-in thick), was poured. The slab was allowed to cure under ambient conditions (no steam). On 10 April, cylinders molded from this batch were tested. Cylinders that had been autoclaved at 103 kPa (15 psi, approximately 120° C) for a period of 30 minutes tested at 24,750 kPa (3,585 psi) and 23,028 kPa (3,340 psi). Cylinders cured at ambient temperatures tested at 2,068 kPa (300 psi). The mix used on the test slab was very fluid; almost 254 cm (10 in) slump. Even this wet, the binder gained strength and the slab was moved in one piece with a front-end loader after 24 hours.

First Pavement Repair Trial

83. At 1000 hrs on 10 April work was begun in charging the pan mixer and loading all of the material for mixing 0.2 m^3 (1/4-cu yd) of material into a concrete bucket to charge the mixer. The mixer started at 1006 hrs. Mixing required 8-9 minutes per 0.2 m^3 batch. The patch was completed at 1036 hrs and the patch was allowed to preset until 1130 hrs. A wooden frame was placed over the patch. The styrofoam "planks" were placed over the top of the frame. By 1107 hrs, the patch was firm enough to support a person's weight. Two steam generators (steam cleaners) were set up to put steam directly on the surface of the patch. The generators were cut on at 1127 hrs. At 1143 hrs, the polystyrene insulation bowed and, in the process of fixing the insulation, it was discovered that the steam had stripped the binder off of the top 6 mm (1/4-in) of the slab. One steam generator was removed and heat-curing continued until 1306 hrs. The test loading with 12,247 kg (27,000 lbs) on an F4 wheel cracked the 18-cm (7-in) thick patch. The wheel also cracked the 23-cm (9-in) thick, 14-day old concrete slab that was used as a form.

84. The cylinders cured with the slab tested at 26,200 kPa (3,800 psi) unconfined compressive strength, but did not have sufficient flexure strength

to survive the loading. The patch failed in flexure. This patch was removed with a jackhammer.

Second Pavement Repair Trial

85. A second trial patch was begun at 1409 hrs. The patch was prepared in three batches and the last batch was placed at 1436 hrs (Figures 6 and 7). Steam was put on the slab only after it had been covered with polyethylene. Steam went on at 1430 hrs (one steamer only). Because the temperature in the slab rose slowly, a second steam generator was added at 1515 hrs. Steam curing continued with short interruptions to check the condition of the slab or to remove test cylinders.

86. At 1711 hrs, the temperature at 5 cm (2-in) depth in the slab was 49° C (120° F). An ambient cured cylinder broke at 2,200 kPa (320 psi) after three hours. At 1732 hrs, a cylinder was removed from the steam frame and broken. It failed at 36,500 kPa (5,300 psi). At 1800 hrs, a second cylinder tested at 39,500 kPa (5,730 psi). The steam was shut off and the frame and plastic were removed. At 1809 hrs, four hours after the mixer was started, the slab was loaded with 12,250 kg (27,000 lb) F4 load cart. No cracking, grooving or rutting was observed. There were only small thermal cracks in the top of the slab. The top 5 cm (2 in) of the slab reached 60° C (140° F), the bottom 5-cm layer reached 49° C (120° F).

Ambient Cured Patch

87. At 0900 hrs on 11 April, a patch was placed at the first location (where the first patch had been dug out). This was allowed to cure without steam. After 24 hours, cylinder tests indicated the patch had achieved 4482 kPa (650 psi) unconfined compressive strength.

Cylinder Tests

88. At 1000 hrs on 12 April, 15 cylinders were prepared and steam cured in a manner similar to the second test slab. They were broken on 13 April and tested at 48,300 - 55,200 kPa (7-8,000 psi) after 28-30 hours.

89. The demonstration showed that useful patches could be prepared using a commercially produced alkali-activated binder. The specifications for the patch material as furnished by the manufacurer are presented in Table 2.

Table 2

Product Designation: PYRAMENT Series 464 Binder Aggregate Mix

19 mm (3/4" Maximum size aggregate - 9.8 sacks (42.6 kg/sack) per cubic meter (7 1/2 sacks (94 lbs/sack) of binder per cubic yard)

38 mm (1 1/2") Slump

2.8 percent entrained air - 2,406 kg per cubic meter (150.2 lbs per cubic foot) weight

30 Minutes working time

Compressive Strength, 10.2 x 20.3 cm (4 x 8 in) Cylinders, kPa (psi)

Age from Start of Mixing	Steam Cured for Up to 1 1/2 Hrs Then in Air		Cured in Ambient air Temp of 22.8°C (73°F)		Cured in Autoclave at 121° C (250° F) for 15 Min,Then in Air at 22.8°C (73°F)	
1 Hr.	35,200	(5,100)	--		38,600	(5,600)
2 Hrs.	42,100	(6,100)	--		44,100	(6,400)
4 Hrs.	44,100	(6,400)	--		48,300	(7,000)
1 Day	46,200	(6,700)	28,300	(4,100)	--	
3 Days	46,900	(6,800)	40,000	(5,800)	--	
7 Days	50,300	(7,300)	65,500	(9,500)	--	
28 Days	53,100	(7,700)	75,900	(11,000)	--	
3 Months	56,500	(8,200)	39,600	(13,000)	--	

Tensile Strength, 10.16 x 20.32 cm (4 x 8 in) Cylinder, kPa (psi)

4 Hrs.	3,400	(500)	--	--

Flexural Strength, 15.2 x 15.2 x 76.2 cm (6 x 6 x 30 in) Beam, Center Point Loading, kPa (psi)

4 Hrs.	4,100	(600)	--	--

Volume Change, ASTM C-157, % Change

28 Days	--	-0.015 in 50% R.H. Air	--
28 Days		+0.010 in Water	

Air Entrained Concrete - Steam Cured, Compressive Strength, kPa (psi)

Age	3.5% Air, 6.4 cm (2 1/2 in) Slump 2,364 kg/cu. meter (147.6 lbs/cu. ft.) 40 min. W.T.*		4.5% Air, 10.2 cm (4 in) Slump 2,294 kg/cu. meter (143.2 lbs/cu. ft.) 70 min. W.T.*	
4 Hrs.	41,400	(6,000)	38,000	(5,500)

NOTE: Higher slump and longer working times require preset period before applicationof heat.

* W.T. = Preset or wait time.

PART VI: SUMMARY AND RECOMMENDATIONS

90. Alkali-activated binders are developing into a family of products that have unique characteristics in terms of their high early strength, high ultimate strength and adaptability in formulation and placement. The increasing amounts of fine-grained reactive alumino-silicate material available from pollution control equipment and the continuing high cost of fuel required to make conventional binders make the use of alkali-activated binders economically attractive. Alkali-activated binders have the potential to become the best and in many cases the most economical binder for routine construction and may evolve into a new generation of building materials.

91. The high strength and versatility make alkali-activated binders a potentially valuable material for military construction and repair. If these binders become common in construction applications (especially in Europe), they may become the material of choice for expedient military construction and repair.

92. Alkali-activated binders deserve continuing attention as they are developing both in the United States and abroad. They may represent the construction material used by our forces as well as an opposing military power. Attention should be directed toward:

- a. Continuing assessment of the state-of-art in alkali-activation technology.
- b. Examination of the techniques that can be employed to produce the heat needed for curing the existing binders.
- c. Examination of additives that can control the set time and improve handling in the available mixes.
- d. Development of preliminary guidelines that can be used in the selection of binders components and fillers/aggregates in the alkali-activated products.

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